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Ambient mixing ratios of nonmethane hydrocarbons (NMHCs) in two major urban centers of the Pearl River Delta (PRD) region: Guangzhou and Dongguan

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Abstract

The Pearl River Delta (PRD) region can be considered one of the most economically developed areas of mainland China. In September 2005, a total of 96 whole air samples were collected in Guangzhou and Dongguan, two important urban centers of the PRD region. Guangzhou is considered the economic center of Guangdong province, and Dongguan is a rapidly expanding industrial city. Here, we report mixing ratios of 50 nonmethane hydrocarbons (NMHCs) that were quantified in the ambient air of these PRD centers. The discussion focuses on understanding the main sources responsible for NMHC emissions, and evaluating the role of the identified sources towards ozone formation. Propane was the most abundant species in Guangzhou, with an average mixing ratio of 6.8 ppbv (± 0.7 ppbv S.E.), compared to 2.5 ± 0.2 ppbv in Dongguan. Toluene was the most abundant hydrocarbon in Dongguan (6.1 ± 0.8 ppbv, compared to 5.9 ± 0.7 ppbv in Guangzhou). Based on an analysis of the correlation between vehicular-emitted compounds and the measured NMHCs, together with the benzene-to-toluene (B/T) ratio, vehicular emission appears to be the dominant source of NMHCs measured in Guangzhou. By contrast, selected species (including toluene) in many of the Dongguan samples were influenced by an additional source, most likely related to industrial activities. A specific B/T ratio (< 0.20) is proposed here and used as indicator of samples strongly affected by industrial emissions. The ozone formation potential (OFP) is calculated, and the role of the different NMHCs associated with industrial and combustion sources is evaluated.

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Keywords: Urban air quality; Nonmethane hydrocarbons; China; Gaschromatography; Ozone formation potential

1. Introduction

The transition to a market economy, which began in the 1980s, makes China one of the world's fastest

growing economies. The number of people living in urban areas has greatly increased, particularly in the past 10 years. In 2000, the gross domestic product of China was 2.6 times higher than in 1990, and 6.4 times higher than in 1980 (China Statistical Year-book, 2005). The growth of the Chinese economy can be clearly seen in the rise in energy consumption since the late 1970s, from about 0.6 billion tons of

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standard coal equivalent (SCE) in 1980 to almost 2.0 billion tons of SCE in 2004 (China Statistical Yearbook, 2005). Several environmental issues are associated with this rapid development, including a severe degradation of the air quality resulting from the sharp increase in anthropogenic pollution emissions (Klimont et al., 2002). Among the different chemical compounds emitted into the troposphere as a result of human activities, volatile organic compounds (VOCs) are particularly important because the chemical reactions involving these species, nitrogen oxides (NO_x), and hydroxyl radicals (OH) in the presence of sunlight lead to the formation of tropospheric ozone (O_3).

China's most developed regions are the urban coastal areas, in particular the Yangtse River Delta (YRD) region and the Pearl River Delta (PRD) region situated in China's fastest growing province of Guangdong. Although the PRD land area is <0.5% of the total Chinese area, its gross domestic product (GDP) is almost 10% of the total (Table 1) and the PRD can be considered the most economically developed area of Guangdong Province. Many high-tech and labor-intensive enterprises operate there, and products such as electronics, toys, textiles, clothing and shoemaking, petrochemical, leather, papermaking, and paper items are manufactured in the PRD.

Several sampling campaigns have been carried out in the PRD during the past years. However, because of the incredibly fast changes experienced by this region, updated studies are constantly needed to characterize the urban air of the different cities located here. When previous studies carried out in the past few years are considered, it should be noted that in most cases, roadside microenvironments, indoor areas, and industrial locations were investigated, rather than the overall ambient air,

with the majority of the studies focusing on the BTEX fraction (benzene, toluene, ethylbenzene, and xylenes) and a few short chain hydrocarbons. The role of the different pollutant sources would be better understood if measurements of a wider variety of species were available. Our research aims to augment this lack of important information. For instance, two previous studies were carried out in Guangzhou. In February 2002, Zhao et al. (2004) measured the BTEX fraction in samples collected in the urban roadside. During the same period, Tang et al. (2005) measured BTEX and two other aromatic compounds in indoor (49 samples) and outdoor (8 samples) areas. In Hong Kong, the BTEX fraction in the overall urban air was investigated by Guo et al. (2004) (selected C_3 – C_5 nonmethane hydrocarbons (NMHCs) were reported) and Ho et al. (2004), while roadside samples were collected by Ho et al. (2002). A comprehensive characterization of the NMHC fraction is rarely available. Chan et al. (2006) presented a wide variety of NMHCs measured in different PRD cities for samples collected in industrial areas. Many NMHCs were also reported for field measurements carried out at different sites in Hong Kong (So and Wang, 2004; Zhang et al., 2007; Guo et al., 2007) and at a polluted rural/coastal site in the PRD (Wang et al., 2005; Guo et al., 2006).

In this study, a comprehensive speciation of NMHCs, halocarbons and other VOCs was carried out in 2005 in the urban areas of two of the most important cities of the Guangdong Province (Guangzhou and Dongguan). Because of the increased levels of tropospheric ozone observed in many PRD cities (Wang et al., 2003, 2006), the reactivity of the different gases toward ozone formation is also evaluated.

Table 1

Area, population, and GDP for Dongguan, Guangzhou, Guangdong Province, and China

	Area (km^2)	Population	GDP (billions USD)
Dongguan City ^{a,c}	2465	7,500,000	27
Guangzhou City ^a	7435	9,943,000	64
PRD ^a	41,700	43,070,000	223
Guangdong Province ^b	177,900	83,040,000	271
China ^b	9,600,000	1,299,880,000	2200

^aZou (2006, personal communication) (2005 data).

^bChina Statistical Yearbook (2006).

^cIncluding the urban area and 32 satellite towns.

2. Experimental

2.1. Site description

The PRD region includes nine different prefecture-level cities composed of an urban center surrounded by a perimeter of districts and/or towns directly administered by the city. Two of these cities are Dongguan and Guangzhou.

Dongguan has experienced rapid economic growth in the past two decades, becoming an important industrial center among cities in the Guangdong Province. It is located on the east side of the Pearl River Estuary, south of Guangzhou and north of Shenzhen ($22^{\circ}39'N$ – $23^{\circ}09'N$, $113^{\circ}31'E$ – $114^{\circ}15'E$). Dongguan is divided into three districts and has direct administration over 32 towns where the majority of the industrial activities are located.

Guangzhou ($22^{\circ}26'N$ – $23^{\circ}56'N$, $112^{\circ}57'E$ – $114^{\circ}03'E$), the capital of Guangdong, is at a higher administrative level than Dongguan. It is divided into 10 districts, and has direct jurisdiction over two county-level cities. Its land area is only 4% that of Guangdong Province yet Guangzhou accounted for 32% of the province's GDP in 2004 (Table 1), and it is, therefore, considered the economic center of the PRD.

2.2. Sampling plan

Individual 21 electropolished, stainless steel, evacuated canisters were used to collect 96 ambient, ground-level whole air samples. A stainless steel bellows valve was slightly opened to fill each canister to ambient pressure in about 2 min at a height of about 2 m.

Of the 96 samples, 48 were collected within the urban area of Guangzhou in September 2005. Sampling locations were selected within six districts of Guangzhou, namely, Liwan, Baiyun, Haizhu, Tianhe, Yuexiu, and Huangpu (Fig. 1). An air sample was collected three times a day (10:00, 14:00, and 18:00 local time) in each location on Thursday, 8 September and Friday, 16 September (total of 36 samples). More intensive diurnal sampling was carried out in the seventh district, Dongshan, where six samples were collected on 8 September at 7:00, 9:00, 12:00, 15:00, 18:00, and 20:00. All 42 samples were filled in parks, gardens or other locations removed from direct VOC sources. Therefore, they are expected to be representative of the average composition of the Guangzhou urban air. Six more

canisters were filled next to a roadside on 8 September at 7:00, 9:00, 12:00, 15:00, 18:00, and 20:00.

The remaining 48 samples were collected in the Dongguan area. Because of the importance of industrial activities in the surrounding areas of Dongguan, samples were collected both within the urban area of the city, and in four satellite towns located around Dongguan's urban center where industrial activities dominate (Fig. 2). A total of 18 canisters were collected in urban Dongguan in three different locations (south side of the city, east side of the city, and Flower market). The canisters were filled three times a day at each site (10:00, 14:00, and 18:00) on Thursday, 22 September and Friday, 23 September 2005. In a more intensive sampling, six samples were collected on 22 September at 7:00, 9:00, 12:00, 15:00, 18:00, and 20:00 at the People's Park in the center of urban Dongguan. Therefore, a total of 24 samples were filled within the Dongguan urban area. Samples were also collected three times a day (10:00, 14:00, and 18:00) on 22 and 23 September in four towns administered by Dongguan: Shilong, Houjie, Changping, and Zhongtang (total of 24 canisters, Fig. 2). To properly characterize the Dongguan Municipality, both the urban samples and the samples collected in the surrounding towns were filled in parks and gardens to avoid direct source points.

To minimize the impact of different meteorological conditions on the ambient levels of VOCs studied in the two PRD cities, the four sampling days were carefully chosen. Sampling was carried out during days characterized by similar meteorological parameters such as temperature, wind speed, wind direction, and relative humidity (Table 2). Moreover, the selected days were representative of the average weather of late summer/early fall in the PRD region. The influence of the boundary layer (BL) height on the measured levels should also be considered when samples are collected at different times. Because of the BL expansion in the morning and collapse during the evening, highly concentrated samples collected early in the morning or late at night could be the result of a reduced BL height. Although no specific information about the time of the BL change in the two PRD cities is known to the authors, 90 of the 96 canisters were filled between 9:00 and 18:00, when the BL height is likely to be fully expanded at this time of year (three of the remaining six samples were collected at 7:00 and the other three at 20:00).



Fig. 1. Location of the sampling sites within the Guangzhou urban area.

2.3. Trace gas analysis

The filled canisters were shipped to our laboratory at the University of California, Irvine and analyzed for carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), 50 NMHCs, 23 halocarbons, 7 alkyl nitrates, and 3 sulfur compounds (OCS , DMS , and CS_2). The gas chromatographic system, quality assurance and quality control description are given in Colman et al. (2001). Briefly, after being cryogenically preconcentrated at -196°C in liquid nitrogen, the sample is vaporized and split to five different column/detector

combinations. Two flame ionization detectors (FIDs; for the detection of hydrocarbons), two electron capture detectors (ECDs; for the detection of halogenated compounds and alkyl nitrates) and a mass spectrometer detector (MSD; for unambiguous compound identification in single ion monitoring) were used. The accuracy and precision are 1% and 2 ppbv, respectively, for both CH_4 and CO , and 1% and 3 ppmv for CO_2 . The accuracy for the NMHCs ranges from 1% to 10%, while the precision of the measurements varies by compound and by mixing ratio. For example, the measurement precision is 2% or 1.5 pptv (whichever is larger) for

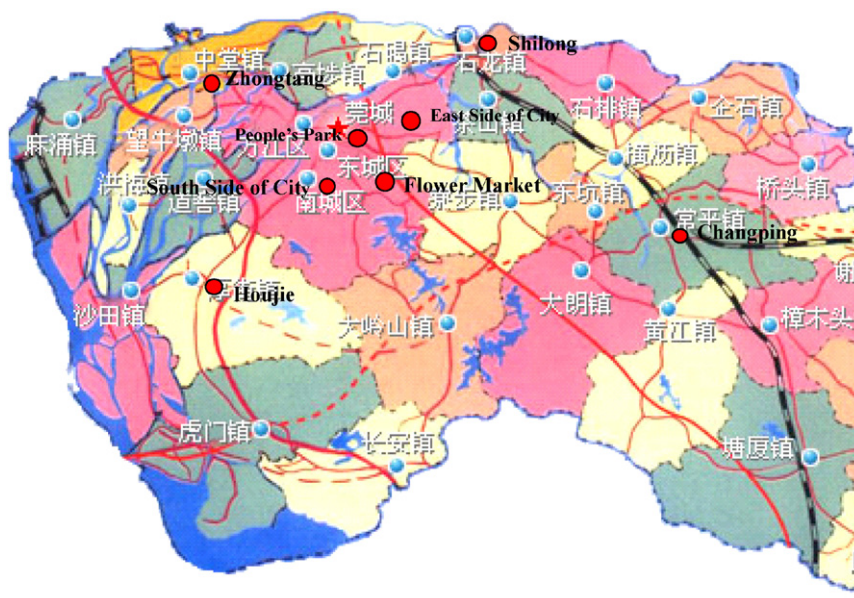


Fig. 2. Location of the sampling sites in Dongguan and its satellite towns.

Table 2
Meteorological parameters recorded during the sampling

	Guangzhou		Dongguan	
	8/9/2005	16/9/2005	22/9/2005	23/9/2005
Max temperature (°C)	33	35	34	32
Min temperature (°C)	25	27	27	25
Avg wind velocity (km h ⁻¹)	4	5	7	8
Wind direction	Northeast	Northeast	North	Northwest
Atmosphere pressure (hPa)	1011	1011	1007	1008
Avg relative humidity (%)	65	66	66	63
Rain fall (mm)	0	0	0	0

the alkanes and alkynes, and 3% or 3 pptv (whichever is larger) for the alkenes. The limit of detection for the NMHCs is 10 pptv.

3. Results and discussion

Although CH₄, CO, CO₂, NMHCs, halocarbons, alkyl nitrates, and sulfur compounds were quantified, the discussion here will focus on NMHCs.

3.1. Ambient mixing ratios and source identification

Table 3 lists the mixing ratios of the NMHCs measured in the ambient air of the two urban centers. The six traffic samples collected in Guangzhou are not included because they are not representative of

the average urban NMHC composition. Therefore, Table 3 includes a total of 42 samples collected in Guangzhou and all 48 samples collected in Dongguan.

Samples from both the urban center and the surrounding towns of Dongguan were averaged together in Table 3 because they are considered representative of the overall air composition of the Dongguan Municipality. In fact, based on averaging the samples collected on 22 and 23 September, the average mixing ratios measured in the satellite towns of Dongguan is not significantly different than in urban Dongguan (Fig. 3). To better evaluate the difference in the hydrocarbons' distribution, the ratio between the average mixing ratio measured in the urban Dongguan and in the surrounding towns was calculated. Forty out of the 50 NMHCs

Table 3

Minimum (min), maximum (max), average (avg), median, and standard error (S.E.) of the VOCs measured in Guangzhou and Dongguan

	Guangzhou (<i>n</i> = 42)					Dongguan (<i>n</i> = 48)				
	Min	Max	Avg	Median	S.E.	Min	Max	Avg	Median	S.E.
CH ₄ (ppmv)	1.932	4.852	2.200	2.072	0.070	1.874	2.733	2.062	1.989	0.027
CO ₂ (ppmv)	352	562	398	393	6	367	550	417	412	5
CO (ppbv)	467	2630	1010	835	80	294	3710	1000	737	108
Ethane	809	3470	1890	1740	102	637	2320	1600	1700	63
Propane	1300	19,800	6790	5650	730	476	8130	2460	2010	198
<i>i</i> -Butane	470	6140	2160	1750	225	193	3360	1070	875	85
<i>n</i> -Butane	756	9770	3500	2880	357	368	6500	1890	1450	165
<i>i</i> -Pentane	539	8570	2470	2020	278	317	4660	1420	1162	123
<i>n</i> -Pentane	220	3830	1120	833	125	123	4950	702	507	104
<i>n</i> -Hexane	136	2250	836	630	92	70	2980	698	518	92
<i>n</i> -Heptane	100	2140	687	487	87	34	3230	620	361	102
<i>n</i> -Octane	29	711	201	153	26	22	950	151	91	24
<i>n</i> -Nonane	23	1070	131	83	26	19	282	81	62	8
<i>n</i> -Decane	18	923	116	78	22	15	263	82	68	8
2,2-DMB	10	148	58	47	6	5	114	36	27	4
2,3-DMB	91	1820	548	440	64	36	702	272	250	23
2-Methylpentane	195	2740	896	780	93	85	2270	674	536	69
3-Methylpentane	121	1870	619	448	66	60	1780	487	362	55
2-Methylhexane	127	1830	614	457	70	59	2400	562	378	77
3-Methylhexane	84	2090	700	513	80	60	3030	668	445	95
2,4-DMP	11	263	88	65	10	8	329	74	58	10
2,3-DMP	21	576	190	141	22	14	854	185	118	27
Ethyne	1710	13,400	4950	4150	478	1020	16,700	4270	3770	412
Ethene	780	11,100	3970	3150	419	645	10,700	3070	2620	271
Propene	119	2210	814	665	90	110	1310	526	472	43
1-Butene	70	1060	368	256	43	38	435	194	172	15
<i>i</i> -Butene	72	1150	367	299	40	57	587	248	231	19
1,3-Butadiene	15	557	162	132	22	16	267	116	114	9
<i>trans</i> -2-Butene	10	1100	243	160	37	25	512	158	138	15
<i>cis</i> -2-Butene	8	943	229	162	31	20	452	156	138	14
Isoprene	180	4460	1630	1470	175	111	4740	676	422	115
1-Pentene	18	541	138	90	20	17	222	88	78	8
<i>trans</i> -2-Pentene	10	816	179	135	27	27	390	146	129	13
<i>cis</i> -2-Pentene	5	431	96	69	14	17	214	80	77	6
2-Methyl-1-butene	22	897	236	148	34	27	513	158	132	16
3-Methyl-1-butene	13	220	66	44	8	10	103	42	38	3
2-Methyl-2-butene	7	990	162	99	29	32	483	176	149	15
α -Pinene	13	615	142	84	23	15	521	126	86	15
β -Pinene	3	50	20	14	2	3	75	20	16	2
Benzene	647	6800	2050	1490	240	274	6450	1260	1050	140
Toluene	716	19,600	5870	4110	736	530	25,300	6130	3950	805
Ethylbenzene	141	4600	1240	742	176	65	7450	1060	745	173
<i>m</i> -Xylene	156	3150	944	603	129	63	3820	939	722	103
<i>p</i> -Xylene	93	1830	595	436	69	47	2130	542	446	61
<i>o</i> -Xylene	101	1770	568	442	68	53	2110	515	402	56
<i>i</i> -Propylbenzene	9	128	38	26	4	3	124	28	24	3
<i>n</i> -Propylbenzene	18	248	77	60	8	10	268	49	40	6
<i>m</i> -Ethyltoluene	41	679	205	142	24	24	481	142	116	13
<i>p</i> -Ethyltoluene	26	344	116	81	12	21	222	69	57	6
<i>o</i> -Ethyltoluene	10	354	78	48	12	6	272	47	38	6
1,3,5-TMB	20	422	109	71	15	11	242	78	69	7
1,2,4-TMB	91	1070	332	269	36	37	510	210	174	12
1,2,3-TMB	26	408	142	90	18	19	186	68	56	6

Units are pptv, unless otherwise specified (DMB: dimethylbutane, DMP: dimethylpentane, TMB: trimethylbenzene).

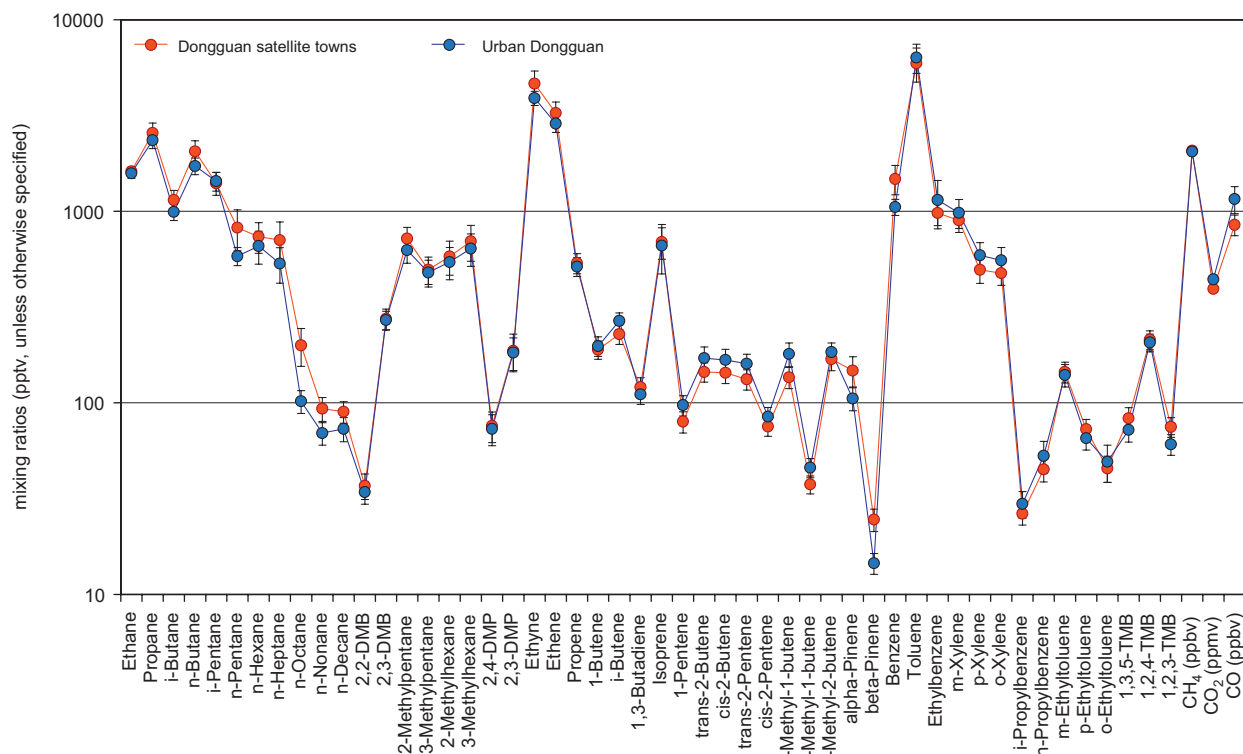


Fig. 3. Average NMHC mixing ratios measured in the Dongguan urban area (24 samples) and in the surrounding towns (24 samples). DMB: dimethylbutane, DMP: dimethylpentane, TMB: trimethylbenzene. The error bars represent the standard error.

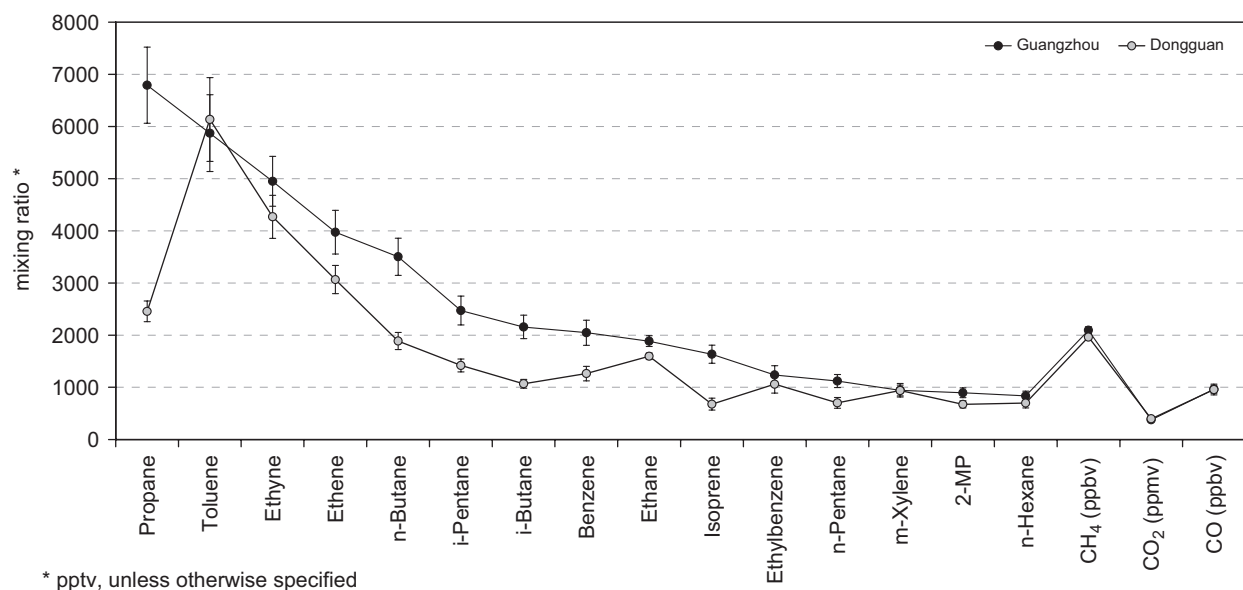


Fig. 4. Average mixing ratio of CO, CO₂, CH₄, and the 15 most abundant NMHCs measured in Dongguan and Guangzhou (MP: methylpentane). The error bars represent the standard error.

measured have a ratio between 0.8 and 1.2, confirming a similar composition of the ambient air measured within the Dongguan Municipality.

Fig. 4 shows the 15 most abundant gases (which are the same for Guangzhou and Dongguan), together with CH₄, CO₂, and CO. Among the most

abundant NMHCs, C₃–C₅ alkanes, isoprene, and benzene show the largest difference between Guangzhou and Dongguan, with average mixing ratios between 1.6 and 2.8 times higher in Guangzhou than in Dongguan. Given the short transport distance between these two PRD cities (50 km), the higher levels observed in Guangzhou compared to Dongguan shows the strength of the emissions in Guangzhou. Propane was the most abundant NMHC in Guangzhou, with an average mixing ratio of 6790 ± 730 pptv S.E. (median of 5650 pptv; Table 3), followed by toluene, ethyne, ethene, and *n*-butane. In Dongguan, the same five NMHCs were the most abundant species, but with a different ranking order. The highest levels were measured for toluene (average of 6130 ± 805 pptv; median of 3950 pptv), followed by ethyne, ethene, propane, and *n*-butane.

It is known that selected compounds are emitted by specific sources and, therefore, they can be used as “tracers”. For example, ethyne’s only recognized source is combustion. Based on a selected subset of the measured gases, an overall good to very good correlation with ethyne was observed in Guangzhou ($R^2 = 0.58$ – 0.92), with the exception of isoprene and ethane (Table 4). The lack of correlation ($R^2 = 0.02$ – 0.26) between ethyne and selected industrially emitted halocarbons (methylene chloride, chloroform, and trichloroethene) ruled out the likelihood that the above good correlations were the result of the co-location of different urban sources. Therefore, combustion appears to be the dominant source of the majority of the NMHCs in the Guangzhou urban area, including alkanes such as propane and the butanes, which are usually not associated with this source. This is consistent with the recognized increase in the number of motor vehicles in Guangzhou (Zhao et al., 2004). A similar situation was observed in Hong Kong, where vehicular emissions were the dominant source, accounting for 50–65% of the total NMHCs measured in three different urban/sub-urban sites (Guo et al., 2007). In Dongguan, a good correlation ($R^2 = 0.59$ – 0.92) with ethyne was found for the alkenes (isoprene excluded), selected alkanes (propane, butanes, and 2-methylpentane), and benzene. A weaker correlation ($R^2 = 0.50$ – 0.57) was found with C₅–C₆ alkanes and with the xylenes, and a lack of correlation ($R^2 = 0.22$ – 0.42) was observed with long chain linear alkanes (*n*-heptane and *n*-octane), toluene, and ethylbenzene. Therefore, sources other than

Table 4

Coefficient of determination (R^2) calculated for selected NMHCs with ethyne and toluene in Dongguan and Guangzhou

	Ethyne ^a		Toluene	
	Guangzhou	Dongguan	Guangzhou	Dongguan
Ethyne	–	–	0.66	0.42
Ethene	0.92	0.92	0.58	0.42
1-Butene	0.59	0.63	0.34	0.28
<i>i</i> -Butene	0.58	0.59	0.27	0.17
1,3-Butadiene	0.74	0.71	0.33	0.12
Isoprene	0.12	0.00	0.16	0.00
Ethane	0.36	0.23	0.14	0.10
Propane	0.64	0.74	0.60	0.42
<i>i</i> -Butane	0.77	0.66	0.77	0.44
<i>n</i> -Butane	0.75	0.62	0.78	0.44
<i>i</i> -Pentane	0.92	0.54	0.60	0.45
<i>n</i> -Pentane	0.89	0.55	0.74	0.64
<i>n</i> -Hexane	0.64	0.50	0.84	0.86
<i>n</i> -Heptane	0.66	0.37	0.96	0.85
<i>n</i> -Octane	0.71	0.22	0.90	0.57
2-Methylpentane	0.87	0.62	0.78	0.75
Benzene	0.72	0.64	0.90	0.59
Toluene	0.66	0.42	–	–
Ethylbenzene	0.73	0.37	0.93	0.76
<i>m</i> -Xylene	0.73	0.57	0.85	0.73
<i>p</i> -Xylene	0.76	0.52	0.89	0.78
<i>o</i> -Xylene	0.76	0.56	0.92	0.75

^aTwo samples with exceptionally high ethyne mixing ratios collected in the two satellite towns of Shilong and Changping on 22 September (14.7 and 16.7 ppbv) were excluded from the correlation.

combustion are contributing to the overall levels of those gases in Dongguan.

Toluene sources in particular have been investigated in previous work (e.g. Ho et al., 2004; Chan et al., 2006; Guo et al., 2006). The high levels of toluene reported in Hong Kong by Ho et al. (2004) were speculated to be emitted by gasoline evaporation because of the high percentage of toluene present in gasoline supplied in Hong Kong (about 20%). Chan et al. (2006) attributed the high toluene levels measured in different PRD cities to industrial activities. Their conclusions were, however, based on samples collected only in industrial locations. Our study gives an excellent opportunity to evaluate the levels and sources of this toxic aromatic compound in the ambient air of two important urban centers. Good correlations ($R^2 > 0.60$) were found in our study between toluene and most of the hydrocarbons for Guangzhou (Table 4). In particular, high coefficients of determination were calculated with ethyne ($R^2 = 0.66$), propane and

the butanes ($R^2 = 0.77$ – 0.78), and the aromatic fraction ($R^2 > 0.85$). As previously discussed, these compounds are associated with a vehicular combustion source in Guangzhou. For toluene, the good correlation with vehicular combustion sources as well as *i*-pentane ($R^2 = 0.60$) indicates that both direct vehicular emission and gasoline evaporation contribute to the toluene levels measured in Guangzhou. On the contrary, weaker correlations ($R^2 < 0.45$) of toluene with ethyne, propane, and *i*-pentane were calculated in Dongguan. The excellent R^2 calculated between toluene and benzene in Guangzhou (0.90) substantially decreased in Dongguan (0.59). This points to the presence of a different (or an additional) source of toluene other than combustion in Dongguan.

Analysis of samples collected at Tai O site, a rural/coastal area located in southwest Hong Kong at the southern tip of the PRD region overlooking the Pearl River Estuary, showed that industrial emissions were the most important source of NMHCs in the PRD area (Guo et al., 2006). However, due to mixing of the sampled air masses, it was not possible to differentiate between the different urban centers. The impact of industrial emissions in Dongguan was evaluated in our study by analyzing the benzene-to-toluene (B/T) ratio for both PRD cities. A value of around 0.5 is found to be characteristic of vehicular emission in many urban areas worldwide, including many Chinese cities (Perry and Gee, 1995; Brocco et al., 1997; Monod et al., 2001; Barletta et al., 2005). The identification of a B/T ratio characteristic of industrial emissions in a major center of the PRD such as Dongguan, could be particularly useful as a tool for identifying a significant influence from a specific source (e.g. industrial emissions) on the overall ambient air. The average ratio (w/w) calculated for Guangzhou is 0.34 (± 0.02 ; 0.17–0.77 range), compared to 0.24 (± 0.03 ; 0.07–0.53 range) in Dongguan. Many samples collected in Dongguan had a ratio below 0.20. This ratio was arbitrarily chosen as the “cut-off” to separate the Dongguan samples in two groups, whereby 22 samples had a B/T ratio below 0.20, and 26 samples had a ratio > 0.20 . Although either reduced benzene or enhanced toluene can lead to a low B/T ratio, the abundance of toluene in Dongguan suggests that low ratios were caused by additional sources of toluene (and possibly other NMHCs), most likely by industries because toluene is used as a solvent in many industrial applications,

and industrial activities are strongly present in Dongguan. As the B/T ratio increases above 0.20, the influence of vehicular emissions becomes increasingly important, though we note that 0.20 is still well below the B/T ratio of 0.5 that applies when vehicular emissions are dominant.

Fig. 5 clearly shows differences between the two groups separated by a B/T ratio of 0.20 (one sample with exceptionally high toluene mixing ratio, 15.5 ppbv, collected at 10:00 on 9 September in the city of Houjie, was excluded from the plots). The weak correlation that was observed above between toluene and many combustion-related compounds in the Dongguan samples (i.e. ethyne, ethene, 1,3-butadiene, and propane; Table 4) substantially improves when the two set of samples are separated (Fig. 5), with greater improvement for the group characterized by a higher B/T ratio (> 0.20). For instance, the R^2 value for toluene and 1,3-butadiene was 0.12 for all the Dongguan samples, compared to 0.35 for B/T < 0.20 and 0.58 for a B/T ratio > 0.20 . This finding supports the importance of a combustion source for the samples with a higher B/T ratio.

The impact of industrial emissions on toluene levels in Dongguan is also highlighted by the good correlation between toluene and methylene chloride (CH_2Cl_2). Methylene chloride is a solvent widely used for many industrial applications. A poor correlation ($R^2 < 0.5$) between CH_2Cl_2 and NMHCs was found in Guangzhou, consistent with combustion as the main NMHC source. On the contrary, good correlation is observed in Dongguan between CH_2Cl_2 and toluene ($R^2 = 0.62$; Fig. 6a), and also between CH_2Cl_2 and C_6 – C_8 linear alkanes (R^2 from 0.58 to 0.61). Moreover, if the samples are separated according to the B/T ratio, a poor correlation ($R^2 < 0.42$) is found between toluene and CH_2Cl_2 for the Dongguan samples with a ratio > 0.20 , and a good correlation ($R^2 = 0.62$) is observed for samples with a ratio < 0.20 (Fig. 6b). The samples dominated by industrial sources were collected within both the Dongguan urban area (16 canisters) and the surrounding towns (6 canisters). This is an additional indication that the ambient air of the Dongguan Municipality is generally well mixed.

In conclusion, our findings suggest that a B/T ratio of 0.20 (or lower) can be used to identify ambient air strongly influenced by industrial emissions within the urban area of Dongguan, and can possibly be used as “indicator” of industrial activities in other centers in the PRD region. This ratio is consistent with the B/T ratio that is

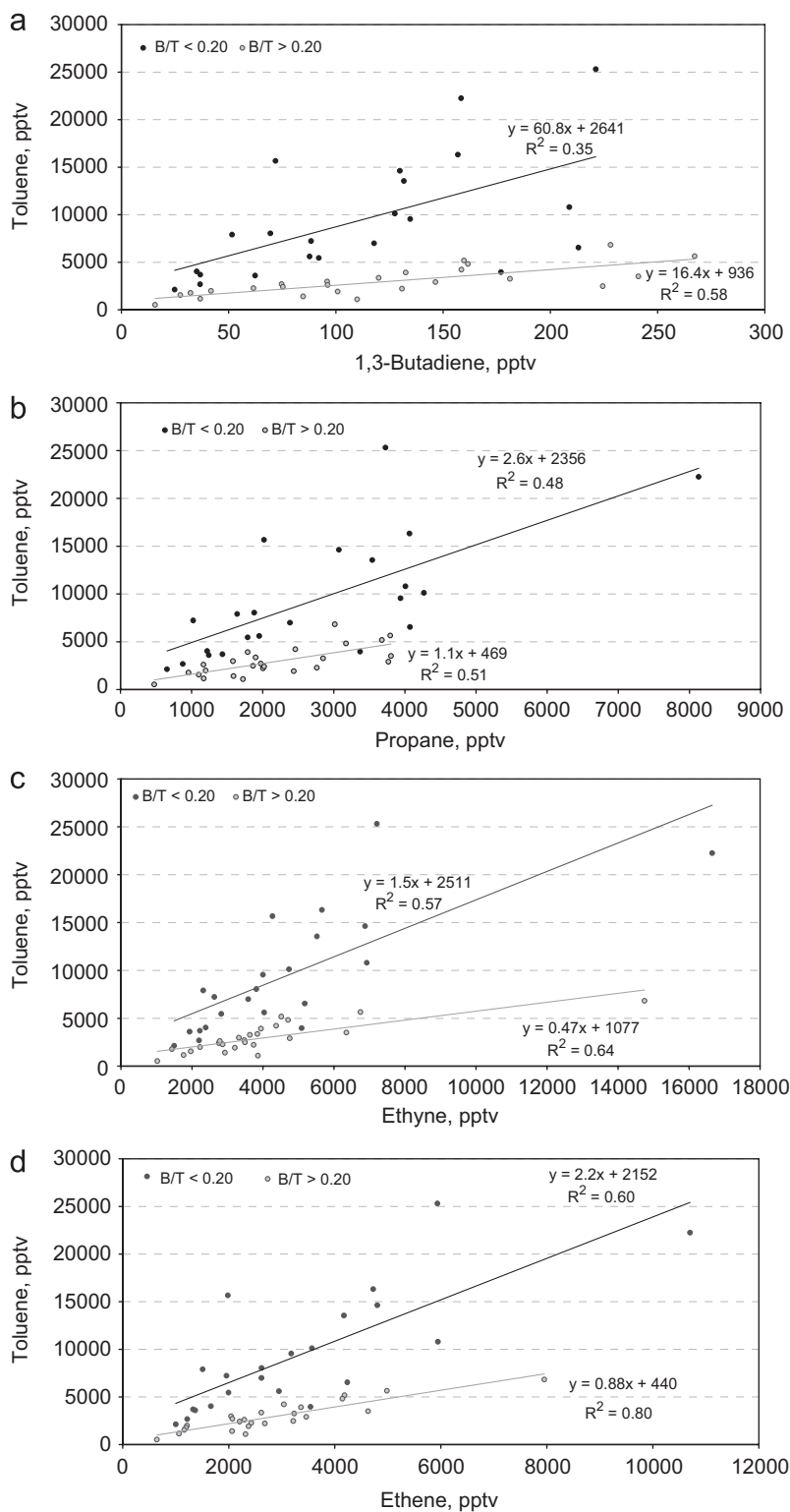


Fig. 5. Correlation plots between (a) toluene and 1,3-butadiene; (b) toluene and propane; (c) toluene and ethyne; and (d) toluene and ethene measured in the samples collected in Dongguan.

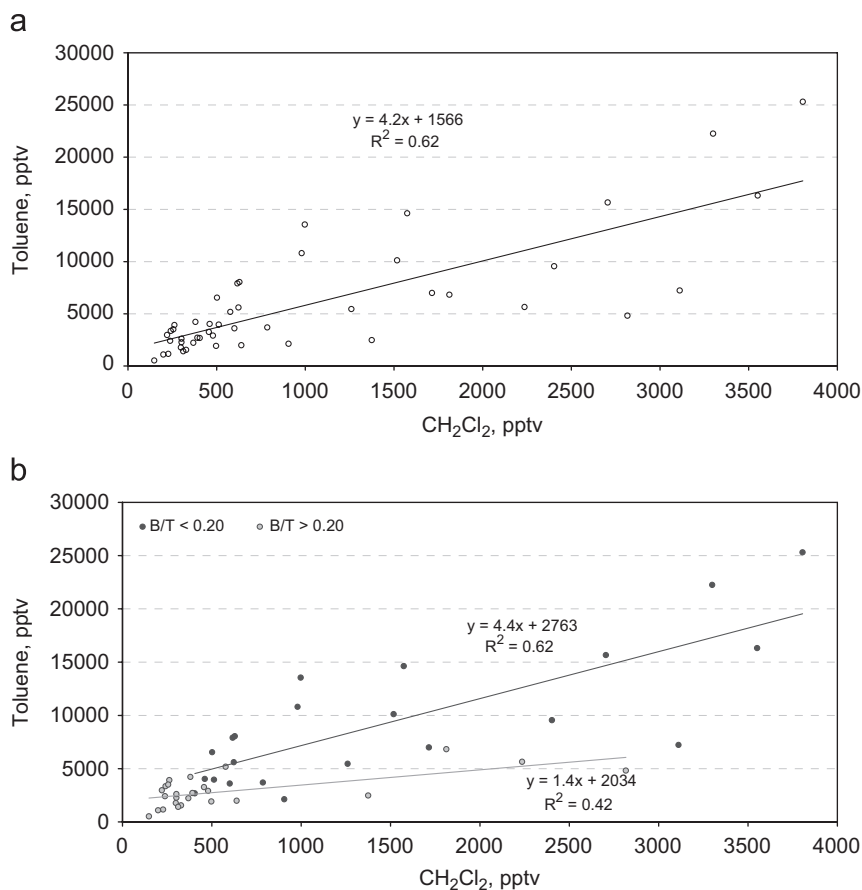


Fig. 6. Correlation between toluene and methylene chloride for all the samples collected in Dongguan (a), and for the samples separated according to the B/T ratio (b).

calculated from the average mixing ratio of benzene and toluene measured by Chan et al. (2006) in the industrial areas of different cities in the PRD (B/T: 0.13–0.15).

3.2. Propane

Propane was the most abundant NMHC measured in Guangzhou, with an average mixing ratio of 6.8 ± 0.7 ppbv (1.3–20 ppbv range; 5.6 ppbv median). It was also highly enhanced in all six samples collected next to a busy roadside (43 ± 15 ppbv; 13–118 ppbv range; 34.5 ppbv median).

The rate constant for the OH–propane reaction is $1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (JPL, 2003) and propane has an OH-lifetime of 10.5 days for an OH concentration of $1 \times 10^6 \text{ molecule cm}^{-3}$. Despite the non-toxic property of this light alkane, elevated mixing ratios can be a cause of concern, for example because of its role in tropospheric ozone formation.

To better assess the possible sources of propane in Guangzhou, cross correlations between propane and other VOCs were investigated. An excellent correlation was found between propane and the butanes ($R^2 = 0.92$; Fig. 7a), indicating a common source for the C_3 – C_4 alkanes. The most likely common emission source is liquefied petroleum gas (LPG) leakage, because propane and the butanes are its three main components. However, propane also shows a very good correlation with ethene and ethyne, two well-known vehicular emission tracers (Fig. 7b). These results strongly suggest that vehicles fueled by LPG are responsible for the elevated propane levels measured in Guangzhou. Although different processes are responsible for the emissions of the species shown in Fig. 7b, the co-location of these emission sources explains the good correlation among these NMHCs. While ethyne and ethene are products of internal combustion, propane is most likely released because of LPG leakage from the fuel

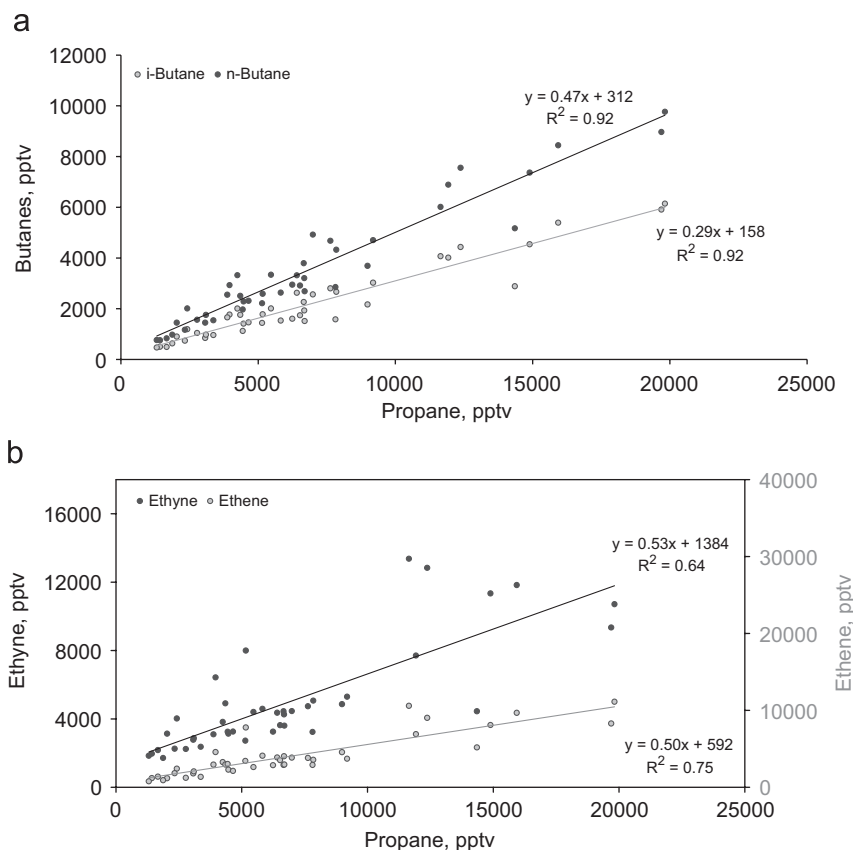


Fig. 7. Correlation of (a) butanes and propane and (b) ethyne and ethene versus propane for the ambient samples collected in Guangzhou.

tank or possibly unburned emission from the tailpipe. The conversion from gasoline-fueled to LPG-fueled vehicles ultimately improves the air quality of an urban area. In fact, the use of LPG reduces the emission of NO_x , CO and many VOCs (Chang et al., 2001; Goekcek and Ertuerk, 2003).

Elevated propane mixing ratios were previously measured in Guangzhou roadside samples. Chan et al. (2006) measured 4 and 8 ppbv propane in two samples collected next to a busy street in Guangzhou in 2000. These levels were higher than propane levels measured in industrial/urban and industrial/rural locations in the PRD, where an average of 2.5 (± 0.3), and 2.1 (± 0.3) ppbv were measured (Chan et al., 2006). However, the enhanced propane was attributed to leakage of LPG from refueling centers for domestic usage rather than to vehicular emissions, mostly because of the limited absolute amount of LPG sales in the PRD (3.5×10^6 tons in 2000), and its limited use as a fuel for vehicles. The average propane mixing ratio measured during our study in Guangzhou is considerably higher than the average level measured by Chan et al. (2006) in

Table 5
Guangzhou car fleet composition, and amount of LPG used in 2004 (Zou, 2006, personal communication)

	Total	LPG	Diesel	Gasoline
Total vehicles	1,700,000			
Bus	20,000	5800	14,200	–
Taxi	16,025	10,453	–	5572
Motorcycle	1,100,000	–	–	1,100,000
Private car	300,000	–	–	300,000
LPG used (tons/year)	120,000			

any of the industrial locations investigated, and data from 2004 show that about one-third of the buses and two-thirds of the taxis circulating in Guangzhou were LPG-fueled (Table 5). It is also important to realize that the amount of gas leaking from LPG tanks or released while vehicles are circulating, rather than the absolute total amount of LPG sold, can strongly affect propane emissions in the urban area. In a different study by Guo et al. (2006), samples were collected at a polluted/rural coastal site in the PRD and air masses originated from

Hong Kong were separated by air masses from inner PRD locations. The higher levels of propane observed in urban Hong Kong with respect to inner PRD regions were attributed to the heavy usage of LPG-fueled taxis and to the widespread domestic usage of LPG in Hong Kong. From their analysis, they concluded that LPG fuel contributes relatively less to the ambient propane concentration in inner PRD. Based on the samples collected during our study within the urban area of Guangzhou, we found instead a significant contribution from LPG-fueled vehicles to the overall ambient levels of propane in Guangzhou. However, the number of LPG vehicles in the PRD greatly increased in the past few years. For instance, Guo et al. (2006) reported that only about 3000–4000 taxis and buses in inner PRD were modified to LPG-fuelled vehicles in 2001. In Guangzhou, about 16,000 taxis and buses were running on LPG in 2004 (Table 5).

Much lower propane levels were measured in Dongguan (2.5 ± 0.2 ppbv average; 2.0 ppbv median), and the LPG sales were also lower in 2004 (55,700 tons in 2004; Zou, 2006, personal communication) compared to Guangzhou. However, the very good correlation between propane with ethene and ethyne in Dongguan ($R^2 = 0.77$ and 0.82 , respectively), together with the excellent correlation with the butanes ($R^2 = 0.92$), strongly suggests that the propane emissions are related to LPG-running vehicles.

Our findings indicate that LPG used as an alternative, cleaner fuel in the PRD, in an attempt to control the increasing emissions associated with vehicular exhaust, is responsible for the high propane levels measured. Therefore, propane emissions could strongly increase in the PRD area if LPG usage increases without a better control of its emissions (and possibly leakage).

3.3. Ozone formation potential

To estimate the role of the different NMHCs towards tropospheric ozone formation, a maximum incremental reactivity (MIR) scale is widely used (Carter, 1994). A dimensionless coefficient (grams of O_3 produced per gram of VOC added to an initial VOC– NO_x mixture) is estimated for each VOC and is multiplied by the VOC concentration to give the expected contribution of each species to local ozone formation (“ozone formation potential”, OFP). Therefore, highly reactive VOCs have high MIR

coefficients. The MIR scale was derived using box model simulations using different VOC scenarios and VOC/ NO_x ratios for the Los Angeles basin, and it was generated to evaluate atmospheric conditions in which ozone production is most sensitive to changes in hydrocarbon emissions rather than NO_x emissions. However, even though this scale does not perfectly fit every urban condition, and needs to be carefully applied, it is widely used to give a general assessment on the importance of the different VOCs on tropospheric ozone formation. We use these calculations to assess the general significance of our observations, focusing on the impact of combustion versus industrial sources toward ozone formation in Dongguan and Guangzhou. Fig. 8 shows the 20 most important gases in terms of ozone formation calculated in Guangzhou and Dongguan (2003 updated MIR: <http://helium.ucr.edu/~carter/reactdat.htm>). In Dongguan, the samples strongly influenced by industrial emissions ($B/T < 0.20$) were separated from the samples where combustion was a dominant source of the measured NMHCs ($B/T > 0.20$).

In Dongguan, ethyne, toluene, and ethene are the most abundant gases (Fig. 4). Whereas toluene has the highest average mixing ratio in the samples with a low B/T ratio (9370 ± 1340 pptv versus 2910 ± 300 pptv for the samples with high ratio), ethyne is the most abundant NMHC in the combustion samples. However, while toluene and ethene are still among the top compounds in terms of ozone formation, ethyne is only ranked 15th (for samples with $B/T < 0.20$) and 14th (for samples with $B/T > 0.20$) because of its longer lifetime and, therefore, lower reactivity (MIR of 1.24 compared to 3.97 and 9.07 for toluene and ethene, respectively). Although toluene is the top species in terms of ozone formation in the two groups of samples collected in Dongguan, a clear difference can be noted in the samples with industrial influence, where toluene accounted for 30% of total OFP versus 16% in the Dongguan samples more strongly influenced by combustion sources (Fig. 8a and b). Toluene was also the most important NMHC in terms of ozone production in Guangzhou with an overall contribution similar to the Dongguan combustion samples (19%, Fig. 8c). In previous studies, So and Wang (2004) and Zhang et al. (2007) also found that toluene and the xylenes were the most important NMHCs towards ozone formation in urban Hong Kong where the reactivity of VOCs was dominated by anthropogenic hydrocarbons.

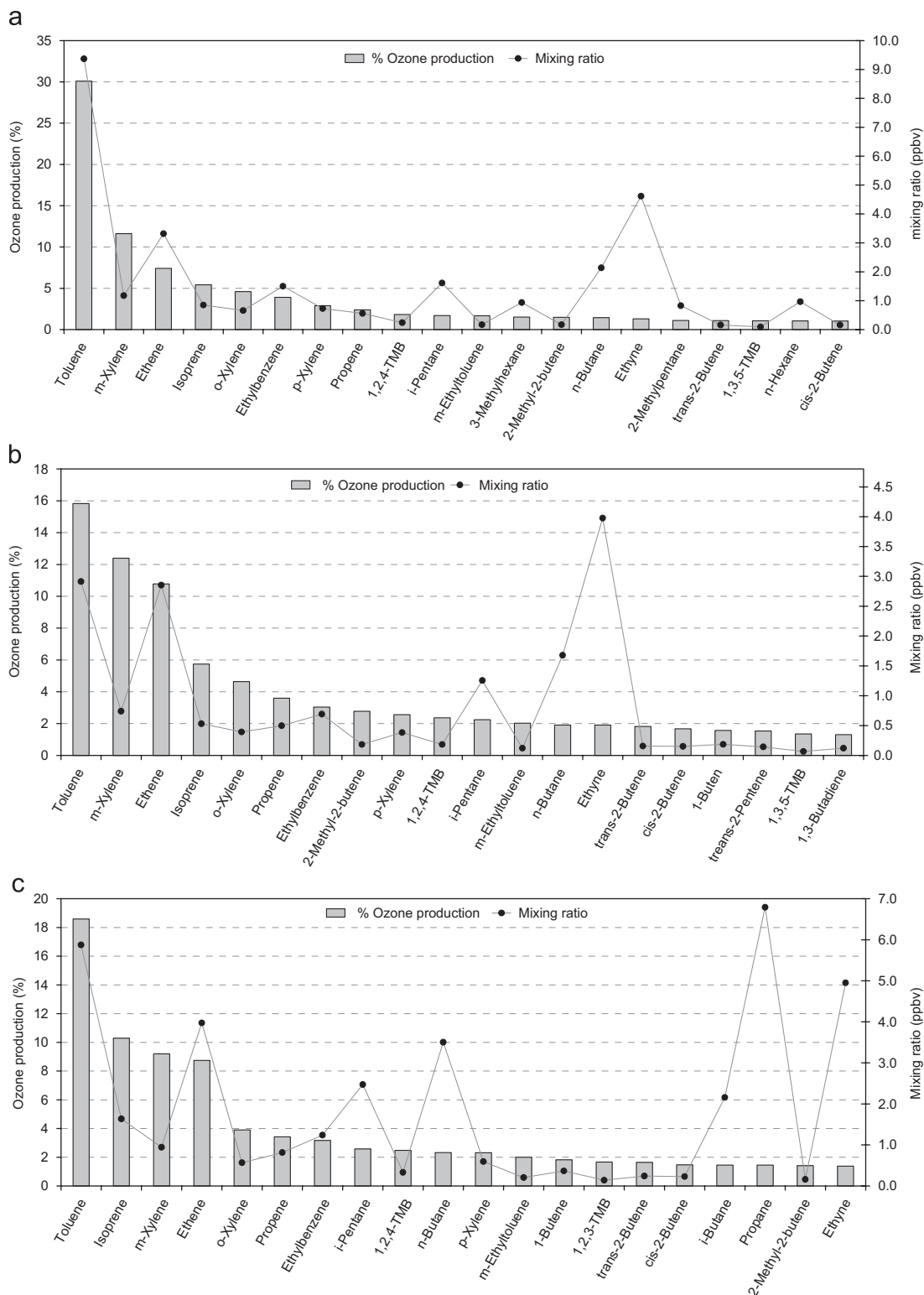


Fig. 8. Twenty most important NMHCs in terms of ozone production (%) calculated for the ambient samples collected in (a) Dongguan (B/T ratio > 0.20); (b) Dongguan (B/T ratio > 0.20); and (c) Guangzhou. The mixing ratio of each species is shown with a circle and reported on the secondary axis. TMB: trimethylbenzene.

Because of the low reactivity of propane (MIR of 0.56 versus 3.97 for toluene), it only accounted for 1.4% of total OFP in Guangzhou, although we notice that it is still about twice the contribution measured in Dongguan (0.6% and 0.8% for the samples with a B/T ratio <0.20 and >0.20 , respectively). Despite propane's low contribution to the overall OFP in the local area, other studies have shown that propane's influence can increase on a regional scale due to its relatively long atmospheric lifetime (Blake and Rowland, 1995; Chen et al., 2001; Luis et al., 2003; Jaimes-López et al., 2005). For example, Chen et al. (2001) found that in Santiago, Chile propane accounted for 5% of OFP on a local scale, compared to 14% on a regional scale. If LPG leakage becomes a relevant source of NMHCs within the PRD region (as it appears to be already the case in Guangzhou), a detailed characterization and quantification of the other species specifically emitted by this source is needed, for example using source profiling. Much more reactive compounds (i.e. short chain alkenes) have been associated with LPG leakage. For example, during a study of LPG leakage in Mexico City, Blake and Rowland (1995) concluded that the amount of ozone produced by emissions of more reactive but less abundant short chain alkenes was comparable to that produced by the much more abundant C_3 – C_4 alkanes. Therefore, the final effect of uncontrolled hydrocarbon release on ozone formation in the PRD needs to be better evaluated.

4. Conclusions

A wide variety of NMHCs together with CH_4 , CO, and CO_2 were measured in the ambient air of two important urban centers in the industrialized PRD region, Dongguan, and Guangzhou, by collecting ground-level whole air samples in September 2005.

Overall higher mixing ratios were measured in Guangzhou compared to Dongguan. The most abundant NMHC measured in Guangzhou was propane, and its main emission source was found to be related to vehicular emissions from LPG-running vehicles. Toluene was the most abundant compound in Dongguan, with both industrial and combustion sources. From cross correlation analyses, vehicular emissions were found to dominate in Guangzhou, while industrial emissions also contributed to the ambient VOC levels in Dongguan.

By analyzing the B/T ratio in Dongguan, samples heavily influenced by industrial emissions could be separated from samples in which combustion dominated. A ratio of 0.20 (w/w) or lower is proposed here to identify industrial sources, while a ratio of about 0.5 is known to be characteristic of vehicular emissions. The ratio of 0.20 could be useful for quickly identifying samples strongly affected by industrial activities, in particular because benzene and toluene can be measured fairly readily with BTEX analyzers.

To investigate the role of industrial emissions versus combustion in terms of ozone production, the OFP was calculated in Guangzhou and Dongguan for samples divided in two groups (B/T <0.20 and B/T >0.20). Toluene accounted for one-third of ozone production in Dongguan samples that were strongly influenced by industrial emissions. In the remaining Dongguan samples and in Guangzhou, toluene contribution to ozone formation was 16–19%. Although propane was the most abundant NMHC measured in Guangzhou, it had a minor role in ozone production, with a contribution of about 1%. However, further analysis of the role of other, more reactive LPG components on the overall OFP in Guangzhou and other PRD centers—where LPG leakage could be a relevant source of NMHCs—is needed.

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